NUCLEOPHILIC ADDITIONS TO UNSATURATED POLYSTERS*

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UNSATURATED polyesters are an important modern group of heterochain polymers and are widely used in the preparation of different copolymers. Very little attention has been paid to other reactions of unsaturated polyesters. We found previously that double bonds in unsaturated polyesters are highly active in nucleophilic reactions. In the presence of alkaline catalysts certain incomplete esters of phosphoric acids combine with them [1]. The capacity of unsaturated polyesters for the diene synthesis was also demonstrated recently [2]. Besides being of theoretical interest, the nucleophilic addition to unsaturated polyesters is also of definite practical interest since the products, saturated polyesters, could be used as plasticizers for polymeric materials in the preparation of varnishes and other coatings.

For the present study we used polyesters based on maleic anhydride and diethyleneglycol. The maleic anhydride was heated with a slight excess of glycol in a nitrogen atmosphere in the presence of hydroquinone at 120–130° for 2 hr. The subsequent heating of 2 hr was at 190°, or under vacuum at 150–180° and a residual pressure of 10–30 mm for 3–5 hr. The polysters produced were colourless viscous resins which were purified by reprecipitation from dioxane solutions by ether and vacuum dried to constant weight at 100°. The molecular weight of the polyesters prepared was calculated from the acid number, as 800 to 3000.

In the first series of experiments we studied the addition of dialkyl phosphorous acid containing from 2–7 carbon atoms in the ether radicals, diethylphosphonacetate and diethylphosphonacetone. The amounts of phosphorus-containing reagents added were calculated for addition to all the double bonds. The reaction was performed in the presence of alkaline metal alkoxides. These were prepared from the alcohol whose radical was contained in the ether groups of the combining reactant. A saturated solution of the alcoholates was slowly added dropwise to a constantly stirred solution of the polyester and phosphorus-containing reagent until further addition caused the heating of the reaction mixture. The greater the molecular weight of the radicals in the ether group of the dialkylphosphorous acids, the slower was the reaction and the greater the amount of alcoholate required to complete it.

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